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Environmental controls on ozone fluxes in a poplar plantation in Western Europe☆

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ABSTRACT

Tropospheric O_3 is a strong oxidant that may affect vegetation and human health. Here we report on the O_3 fluxes from a poplar plantation in Belgium during one year. Surprisingly, the winter and autumn O_3 fluxes were of similar magnitude to ones observed during most of the peak vegetation development. Largest O_3 uptakes were recorded at the beginning of the growing season in correspondence to a minimum stomatal uptake. Wind speed was the most important control and explained 44% of the variability in the nighttime O_3 fluxes, suggesting that turbulent mixing and the mechanical destruction of O_3 played a substantial role in the O_3 fluxes. The stomatal O_3 uptake accounted for a seasonal average of 59% of the total O_3 uptake. Multiple regression and partial correlation analyses showed that net ecosystem exchange was not affected by the stomatal O_3 uptake.

1. Introduction

Tropospheric ozone is a very strong oxidant, with the potential to damage human health, and vegetation functioning (Fowler, 1992; Lefohn, 1992; Wittig et al., 2007; Royal Society, 2008). Over the last 100 years tropospheric ozone pollution has significantly increased (Vingarzan, 2004; Derwent et al., 2007), and $[O_3]$ is predicted to continue rising in the next decades (IPCC-DDC, 2004; Vingarzan, 2004; Royal Society, 2008). Importantly, because of a more stringent regulation in the emission limits of ozone precursors in both the USA and Western Europe, peak ozone concentrations are decreasing in these areas (Vingarzan, 2004; Solberg et al., 2005; Derwent et al., 2007; Jenkin, 2008; Lefohn et al., 2008). Background concentrations are however increasing due to the transport of precursors from the developing world (NEGTAP, 2001; Vingarzan, 2004; Dentener et al., 2006; Davis et al., 2010). These background concentrations are forecast to increase to more than 60 ppb over the next century (IPCC-DDC, 2004) making it extremely challenging to maintain clean air standards (e.g. $[O_3] < 80$ ppb, IPCC, 2001) in densely populated areas (IPCC, 2001; Vingarzan, 2004). The observed increase in $[O_3]$ has already been proved to affect agricultural yield (Benton et al., 2000; Fumagalli et al., 2001), and to lead to biomass/yield reduction in crops in Europe (Mills et al., 2011), potentially reducing the global carbon sink of terrestrial vegetation (Sitch et al., 2007).

Within Europe, high levels of radiation and warmer temperatures, together with the significant anthropogenic sources of ozone precursors, could make the southern ecosystems among the most exposed to O_3 (Cieslik and Labatut, 1997; Nolle et al., 2002; Paoletti, 2006; Manes et al., 2007). However, as ozone impact on vegetation depends on the ozone entering the stomata and oxidizing plant tissues, stomatal ozone uptake better describes the possible effect to the vegetation than ambient ozone concentrations (Emberson et al., 2000; Uddling et al., 2004; Matyssek et al., 2007). Stomatal ozone uptake is the highest under high soil water availability, and consequently ozone can be more damaging in non-water limited ecosystems in Central and Northern Europe (Emberson et al., 2000; Cieslik, 2009; Karlsson et al., 2009; Marzuoli et al., 2009; Zapletal et al., 2011), even with lower $[O_3]$ (Emberson et al., 2000; Mills

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et al., 2011). However, long-term ozone flux measurements of vegetation are still not very frequent (Fowler et al., 2001; Mikkelsen et al., 2000, 2004; Cieslik, 2009; Mills et al., 2011; Rannik et al., 2012), leaving uncertainties about the impact of this pollutant on net ecosystem exchange (NEE) and on plant productivity. In general, the majority of the studies on ozone impacts on vegetation have been carried out in controlled environments where plants are subjected to ozone treatments (e.g. Bortier et al., 1999; Bortier et al., 2000; Novak et al., 2003, 2005; Karlsson et al., 2003a; Wittig et al., 2007; Bussotti et al., 2011). Ideally, ozone impact should be studied under natural conditions (Pilegaard et al., 1998; Kolb and Matyssek, 2001; Gerosa et al., 2003; Fares et al., 2010a). However, such conditions make it a challenge to separate the impact of ozone on carbon assimilation from other factors (such as drought and temperature stress).

The impact of ozone on vegetation has usually been quantified using the AOT40 index, which sums the differences between the hourly mean $[O_3]$ above 40 ppb during daylight hours (Appendix A, Kärenlampi and Skärby, 1996). A more valid approach is to define the amount of ozone entering the leaves through the stomates (Fuhrer, 2000; Emberson et al., 2000; Matyssek et al., 2007; Tuovinen et al., 2007). This stomatal ozone uptake has been described with different criteria in the literature, such as the accumulated stomatal fluxes (AF_{ST}, Mills, 2004; Karlsson et al., 2004; currently indicated as $POD_{Ygen,}$ ICP, 2004), leaf cumulative uptake (CUO) over a threshold (for example cumulative ozone uptake above 1.6 nmol $m^{-2}s^{-1}$ (CUO>1.6, Karlsson et al., 2003b, 2004), and accumulated ozone dose (AOD) (Pollastrini et al., 2010).

Among different plant species, fast-growing poplars are especially susceptible to ozone impacts, because of the high stomatal conductance and thus high ozone uptake (Pye, 1988; Bortier et al., 1999; Novak et al., 2003, 2005). Several studies reported that ozone damage affects the photosynthetic apparatus, leading to visible leaf injury, damage to photosystems and growth reduction in poplar (Bortier et al., 1999, 2000; Oksanen et al., 2001; Fares et al., 2006; Marzuoli et al., 2009; Pollastrini et al., 2010; Bussotti et al., 2011). The sensitivity of poplar to ozone makes the investigation of the environmental controls on ozone uptake particularly relevant. The aim of this study is to investigate the environmental controls on ozone fluxes in a high-density poplar plantation, to quantify the stomatal ozone uptake, and the effect of this ozone uptake on NEE during the growing season.

2. Materials and methods

2.1. Site description

An eddy covariance (EC) tower was installed in a poplar plantation in Lochristi, Belgium (51°06′44″ N, 3°51′02″ E) in spring/summer 2010. The plantation (18.4 ha) was established in April 2010 with different poplar clones of *Populus deltoides, P. maximowiczii, P. nigra,* and *P. trichocarpa*, and interspecific hybrids. The climate is maritime with long-term average annual temperature of 9.5 °C, and precipitation of 726 mm that is uniformly distributed over the year (Royal Meteorological Institute of Belgium, http://www.meteo.be). During the second growing season (2011) after the establishment of the plantation, the canopy height increased from 2.4 ± 0.07 m in April to 4.6 ± 0.14 m in October. The understory of the plantation was typically composed of bare ground with few weeds, mostly thistles. More details on the plantation establishment and development, and on the management of the site, etc. are provided in Broeckx et al. (2012).

2.2. Eddy covariance (EC) system

The EC system was composed of a 3-D sonic anemometer (CSAT 3-D, Campbell Sci., UT, USA) and of several fast-response analyzers, including a LOZ-3F O_3 analyzer (Drummond Technology Inc., Ontario, Canada) and a CO_2/H_2O infrared analyzer (LI-7000, LI-COR, Lincoln, NE, USA). The sonic anemometer was used to calculate the momentum and the sensible heat fluxes. More details on these analyzers are presented in Zona et al. (2013a) and Zona et al. (2013b). The LOZ-3F O_3 analyzer is based on chemiluminescence with Eosin-Y dye (Ray et al., 1986; Topham et al., 1992; Rannik et al., 2012) circulated continuously through a peristaltic pump in the sample cell, and measures O_3 mixing ratio at a 10 Hz sampling frequency. The instrument performs an automatic zero check every hour for about 10 s, then saves the signal acquired during this zeroing mode, and subtracts it from the signal during the following measuring mode. After the zeroing correction, the instrument applies the appropriate calibration factors to output the final corrected mixing ratio (in ppb). A slow response O_3 analyzer (API 400E, Teledyne Instruments, CA, USA) was used continuously to monitor $[O_3]$, which was then compared with the concentrations measured by the LOZ-3F, to control whether any drifting occurred in the signal of the LOZ-3F. The API was calibrated every six months by the Flemish Environment Agency (VMM).

The LI-7000 CO_2/H_2O analyzer was used to measure CO_2 and H_2O mixing ratios, to calculate CO_2 fluxes (NEE) and latent heat (LE) fluxes. Two sampling lines (Teflon tubing about 12 m long and 8 mm inner diameter) were used for the EC system, one for the LI-7000 and another separate line for the two O_3 analyzers (API and LOZ-3F). The two inlets were positioned about 10–15 cm from the center of the sonic anemometer. A 1 μm teflon filter (Gelman) was placed 10 cm after the inlet of the sampling line of the LI-7000. No filter was placed in front of the inlet line of the O_3 analyzers. A coarser filter (20–30 μm, Zitex) was placed in front of the inlet of the LOZ-3F analyzer, and of the API analyzer (5 μm, Savillex), to avoid contamination of the cells. The flow of the main line of the two O_3 analyzers was 20–27 l min^{-1}. As described in Pilegaard et al. (1998), the flow rate used was sufficiently high to maintain a turbulent flow needed to limit possible errors due to tube attenuation (e.g. Reynolds number $Re \geq 3000$, Lenschow and Raupach, 1991). A mass flow controller was used to regulate the flow through all these sampling lines. Prior to the inlets of the two instruments, a Teflon manifold was used to split the air sampled into three parts, as described in Pilegaard et al. (1998); one line was connected to the slow response API analyzer (with flow of about 0.76 l min^{-1}), one to the LOZ-3F (with a flow of about 1.9 l min^{-1}), and the last one was used as a bypass and regulated with a mass flow controller. After the splitting of the flow, the outlets from the instruments were connected again to the main flow outlet. The flow meter inside the LOZ-3F was continuously operated and monitored, assuring a constant and stable flow which, together with the mass flow controller, prevented pressure fluctuations. The LOZ-3F measures cell pressure and temperature, and provides actual mixing ratio thus not requiring any further temperature and vapor density corrections. A buffer volume was placed between the main flow outlet and the pump to dampen the fluctuation of the pump.

2.3. Data processing and filtering of the $[O_3]$ and O_3 fluxes

EdiRe (R. Clement, University of Edinburgh, U.K.) and EddyPro (LI-COR, Lincoln, NE, USA, Fratini et al., 2012) were used for the computation of the fluxes of CO_2, latent heat (LE), sensible heat (H), and momentum. EddyPro was used to calculate the O_3 fluxes. The cross-comparison of LE and CO_2 fluxes calculated using these two software packages (EdiRe and EddyPro) showed very similar results, within 1–2% (data not shown). Consequently, CO_2 fluxes (NEE) calculated using EdiRe (Zona et al., 2012, 2013), and O_3 fluxes calculated using EddyPro were used in this paper.

The mean lateral and vertical velocity components were set to zero by application of a two-component rotation. The maximum cross covariance function (within 30 min averaging time) was used to determine the lag time for O_3, which was about 2 s. A drop-out filter was applied to remove the zeroing periods (10 s every hour) from the raw 10 Hz data. These removed data accounted for a total of only one day per year, limiting biases to the flux computation. An additional pre-processing routine was applied to remove any drift in the $[O_3]$ of the fast-response analyzer. The $[O_3]$ measured by LOZ-3F was compared to the $[O_3]$ measured by the API analyzer (both measured at 5.8 m above the surface from January to 31 August 2011, and at 6.6 m thereafter), and the appropriate offsets and multipliers were applied to the half-hourly averaged 10 Hz data. This calibrated 10 Hz dataset was then used for the final O_3 flux calculation. As the reaction cell of the LOZ-3F contains a liquid solution of Eosin-Y, eliminating water vapor interference, and as the $[O_3]$ were expressed as mixing ratios, i.e. related to dry air, no Webb, Pearman and Leuning (WPL, Webb et al., 1980) correction was needed, as described in Ibrom et al. (2007). Frequency response correction was performed according to Moncrieff et al. (1997), which is an analytical correction modified from the Kaimal formulation (Kaimal et al., 1972). A high-pass filtering correction, as described in Moncrieff et al. (2004), was applied to the O_3 fluxes in the low frequency range (high-pass filtering effect). A low-pass filtering correction was applied as described in Ibrom et al. (2007), and a sensor separation correction according to Horst and Lenschow (2009).

Data were removed if they matched one of the following filtering criteria: during malfunctioning of the instrument (22% of the entire dataset), during calibration, replacement of the filters, and maintenance of the instrument (which together accounted for ∼0.03% of the data), when the half-hour average $[O_3]$ presented more than four spikes (when the standard deviation was >8, ∼0.03% of the data), when the $[O_3]$ was more than 500 ppb (unrealistic values, ∼2% of the data, when the wind direction was outside of the footprint of interest (i.e. >250 and <50°, 35% of the data). As no standardized gapfilling methodology has been developed for eddy covariance O_3 fluxes, the fluxes were gap-filled using a feed-forward back propagation Artificial Neural Network (ANN) (nntool on MATLAB, 2011; Mathworks, Natick, Massachusetts, USA) as described in Papale and Valentini (2003). The meteorological variables used as input for the ANN were: air temperature (air T), relative humidity (RH), wind speed, rainfall, short-wave and long-wave radiation, vapor pressure deficit (VPD), and [O_3]. The ANN had one layer (and 10 neurons) and was trained with 60% of the data and validated with 20% of the data; another 20% of the data was used for independent testing. The training data were used to build the model, which were then used to gap-fill the entire dataset; the validation and independent test data were not used to build the model, but used to check the performance of the gap-filling procedure. The training and validation presented $R^2 = 83\%$ and 86%, respectively. Because of good performance of the model, the chosen percentage of training and validation data were considered reasonable. The data cleaning and gap-filling of the slow response analyzer were performed according to the following procedure: negative [O_3] (caused by malfunctioning of the instrument) were removed and if the resulting gaps were equal to or less than 3 h, the [O_3] were gap-filled by linear interpolation; for gaps longer than 3 h, the gaps were replaced by the [O_3] measured at a nearby station (Admiraaldreef, Destelbergen, Belgium, Flemish Environment Agency, VMM), 7.5 km from our research site and in a similar rural setting. The stomatal uptake (indicated as F_{O3ST} hereafter) estimation and data filtering are described in Appendix A.

Concentrations of NO and NO_2 were measured in three stations in the proximity of Gent (i.e. Baudelostraat in Gent; Admiraaldreef in Destelbergen; Schuitstraat in Sint-Kruis-Winkel), using a TRACE Level NO_x Analyzer (Model 42i-TL, Thermo

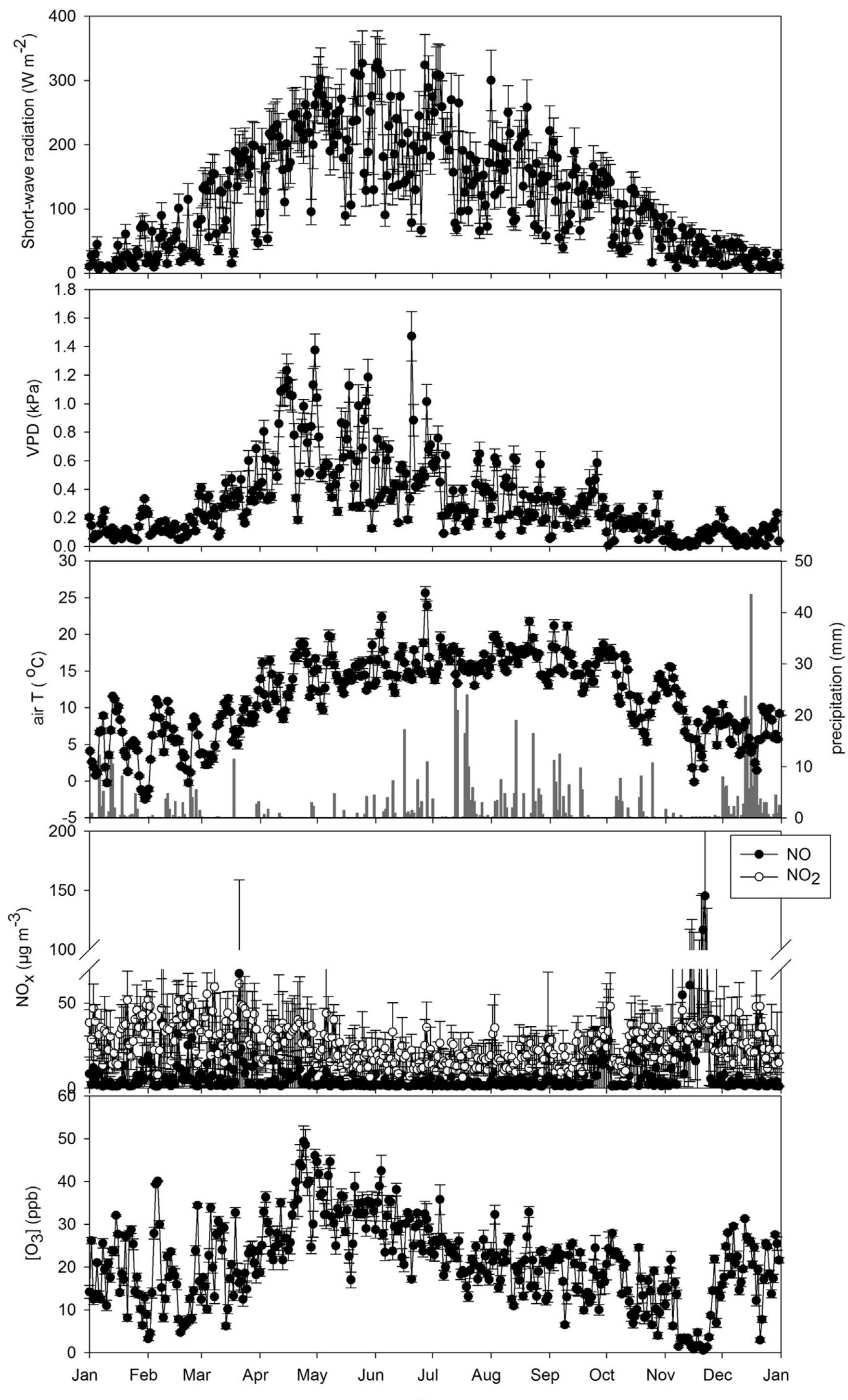

Fig. 1. Seasonal trend in daily averaged short-wave radiation (W m^{-2}), daily averaged vapor pressure deficit (VPD, kPa), daily averaged air temperature (air T, °C) and daily total rainfall (mm), daily averaged NO_2 and NO (average from three stations: Baudelostraat, Gent; Admiraaldreef, Destelbergen; Schuitstraat in Sint-Kruis-Winkel, Belgium), and daily averaged [O_3] (at the field site) in 2011.

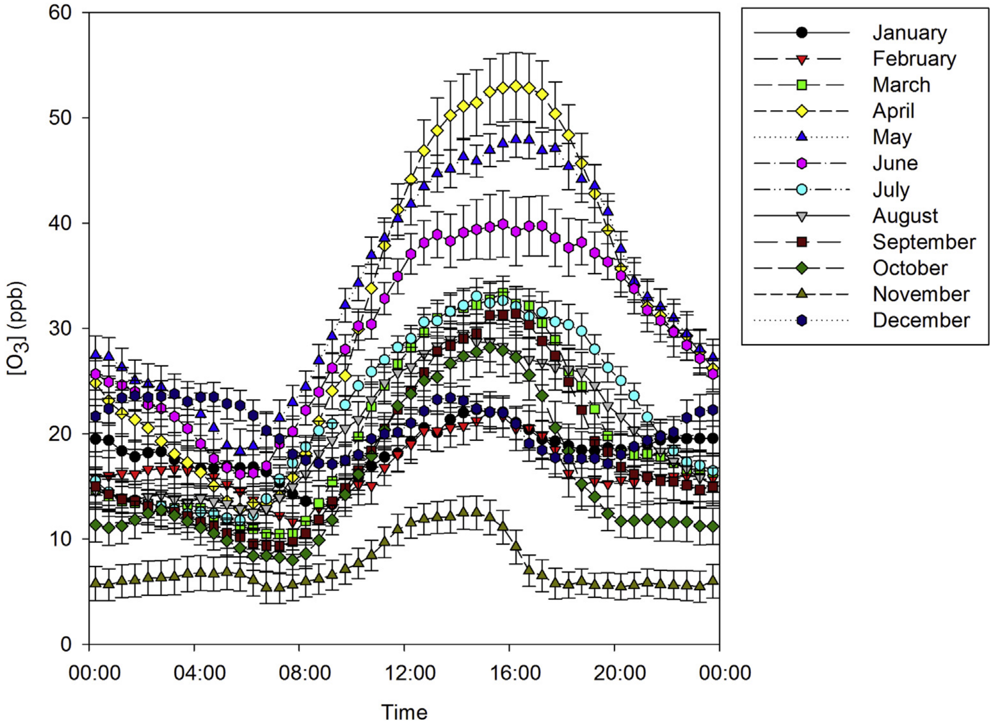

Fig. 2. Average diurnal trends in ozone concentrations ($[O_3]$ ppb) during each of the indicated months. Displayed are ensemble averages and their standard error of the mean.

Scientific Waltham, MA, USA), at about 3 m above the ground, by the Flemish Environment Agency (VMM). The Admiraaldreef and Sint-Kruis-Winkel were in more rural settings than Baudelostraat. The concentrations of NO_x reported in this paper are averages of the measurements in these three stations.

2.4. Statistical analysis

The non-gap-filled ozone fluxes and the deposition velocity (defined as $-F_{O_3}/[O_3]$), were modeled as a function of several environmental variables (air T, RH, VPD, wind speed, short and long-wave radiation) using a general linear model, GLM (Systat version 13, Systat Software Inc., 2002) to test the importance of each variable as control on the fluxes and on the deposition velocity. We performed this analysis on the entire dataset (daytime and nighttime data together) and on the data from daytime and nighttime separately (when short wave radiation was either ≥ 20 W m^{-2} or < 20 W m^{-2}). These analyses were performed on the ozone fluxes and the deposition velocity averaged on a half-hour time scale. The impact of F_{O3ST} was estimated using multiple regression and partial correlation analyses of the residuals from 14 days, derived from a non-linear light-response fits of NEE (see Appendix A for more details). For this analysis a Michaelis–Menten type light response model was used as described in Pilegaard et al. (2011).

3. Results

3.1. Ozone concentration and environmental conditions

The annual course of the daily averages of short wave radiation, air temperature, precipitation, VPD, and concentrations of NO_x and O_3 is shown in Fig. 1. The environmental conditions in April and May 2011 were abnormally dry, with a precipitation (9 mm and 16.8 mm in April and May, respectively) much lower than what usually observed in this area (e.g. the ten year mean of 32.1 mm and 42.1 mm in April and May, respectively). As low precipitation is usually related to high ozone production (Comrie, 1990; Davis et al., 2010), the abnormally dry weather conditions during spring contributed to the fairly high $[O_3]$ (Fig. 1). A spring maximum in $[O_3]$ is typical of background sites in the Northern Hemisphere (Scheel et al., 1997; Angle and Sandhu, 1989; Meagher et al., 1987), where the absence of a summer peak may indicate low influence from the local photochemical ozone production from precursor emission (Hough and Derwent, 1990).

However, the difference between the mean diurnal minimum and maximum $[O_3]$ in our field site was 30 ppb or larger during June–August (Fig. 2), much higher than the 10 ppb observed in conditions not affected by local combustion (Mikkelsen et al., 2004). A spring $[O_3]$ peak has also been related to the photochemical reaction of NO_x originating from combustion processes, with increase in solar radiation during spring (Dibb et al., 2003). On the other hand, the long-term (ten years) $[O_3]$ data from another monitoring site in Belgium (Brasschaat), about 60 km from this field site, showed a summer maximum in $[O_3]$ (Neirynck et al., 2012). This suggests that abnormally dry conditions in spring 2011 may have led to unexpectedly high $[O_3]$. An early season $[O_3]$ peak may

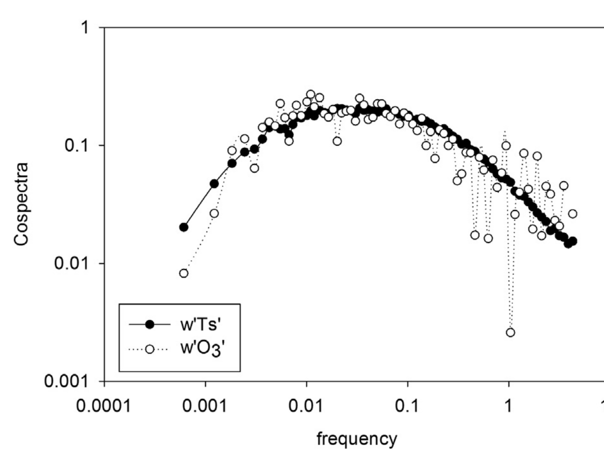

Fig. 3. Cospectra of the fluctuation in vertical wind velocity and in the sonic temperature (w'Ts') and in O_3 (w'O_3') averaged for June–July 2011 (in logarithmic scale) as function of the sampling frequency (Hz).

potentially be very damaging to the vegetation, if it occurs when vegetation is not water limited and therefore stomatal O_3 uptake is maximum (Novak et al., 2005). The maximum [O_3] recorded in our field site was 90.8 ppb on the 24 of April 2011; we investigated the leaves for visible symptoms of O_3 damage. No leaf damage was observed during the measurement period. In November a sudden drop in [O_3] and minimum O_3 fluxes were coinciding with a peak increase in [NO] (Fig. 1). This increase in [NO] was probably linked to the strong ground surface inversion, which resulted in a minimum boundary layer depth during intense local traffic (L. Verlinden, VMM, personal communication).

3.2. Total, stomatal O_3 fluxes, & deposition velocity

Cospectral analysis was used to assess the performance of the LOZ-F instrument for eddy covariance, which revealed some noise in the mid to high frequency part of the spectra, but reasonable comparison with the cospectra of w'Ts' (Fig. 3). The temporal data coverage of the O_3 fluxes (F_{O3}) after filtering was 41%. The seasonal trend in the daily averaged gap-filled total O_3 fluxes (with the percentage of data coverage) and deposition velocity are shown in Fig. 4. Generally, the O_3 fluxes were the most negative from April to July and closely related to the [O_3] (Fig. 1). Substantial O_3 fluxes

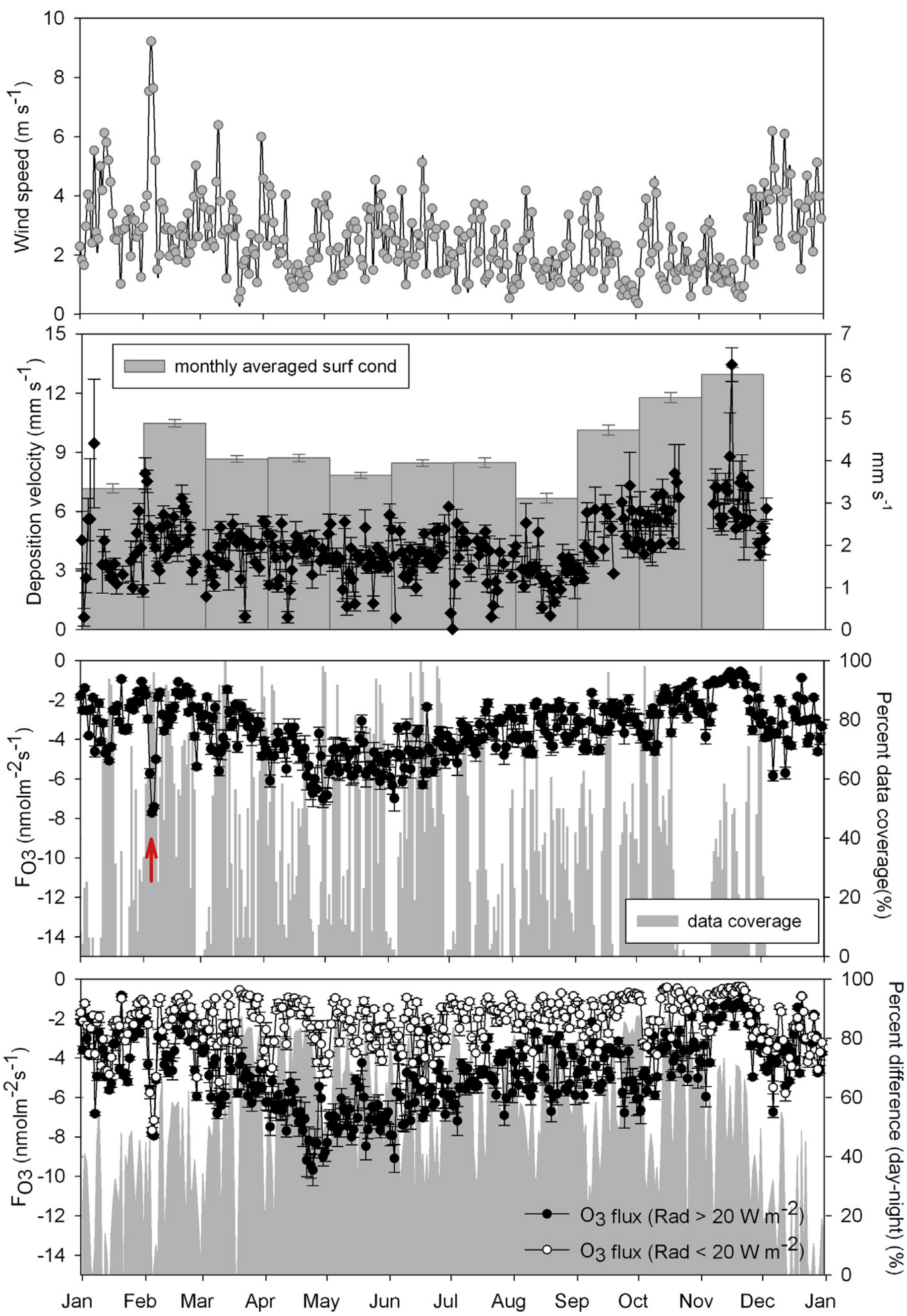

Fig. 4. Wind speed, deposition velocity (not gap-filled, averaged in daily and monthly time scales), daily averaged gap-filled O_3 fluxes (with the percentage of data coverage), gap-filled O_3 fluxes averaged during daytime and nighttime (solar radiation >20 W m^{-2} or <20 W m^{-2}, respectively), and their percentage difference (area plot). Note the substantial O_3 sink when temperature was below freezing from 4 to 6 February (red arrow). Displayed are averages and standard errors of the means (monthly averaged deposition velocity n = 407, 821, 613, 567, 728, 715, 431, 494, 529, 514, 381, 63 for each month from January to December). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were observed when the vegetation was not active yet, with a peak flux in co-occurrence of high [O_3] (4–6 February) during a storm (Fig. 1) and with a wind speed > 7 m s^{-1} (Fig. 4). On 4–6 February, because of the low temperature and radiation (below freezing air temperatures and short wave radiation below 100 Wm^{-2}, Fig. 1), the high [O_3] was probably resulting from the intrusion of stratospheric O_3 into the troposphere (Weber and Prevot, 2002; Cieslik, 2009). The O_3 fluxes (Fig. 4) observed in January–March (when the vegetation was not active yet, and the stem area index (SAI) was about 0.33 ± 0.19 m^2 m^{-2} (Broeckx, personal communication) had comparable rates to the ones observed during the growing season with substantial canopy development (with maximum seasonal leaf area index (LAI) of about 2.5 ± 1 m^2 m^{-2}). The relevance of the stomatal uptake varied considerably during the season (Fig. 5), accounting for about 39% of the total O_3 flux in April, 42% in May, increasing to 65% in June, 72% in July, and 77% in September, decreasing again to 59% in October. The decrease in VPD from June onwards together with the increase in LAI increased the importance of the F_{O3ST} later in the summer (Fig. 5). Generally, the F_{O3ST} was at maximum around noon (Fig. 5), while the [O_3] was at maximum early in the afternoon (around 16:00, Fig. 2). Monthly averaged deposition velocities reached maximum values in February (4.9 ± 0.1 mm s^{-1}), and in October and November (5.5 ± 0.1 mm s^{-1} and 6.0 ± 0.2 respectively, mean ± st. errors, see Fig. 4), before canopy development and after leaf loss.

The non-stomatal uptake increased during daytime (most evident in March, Fig. 6). The controls on the non-stomatal uptake were investigated by examining the environmental controls on O_3 fluxes and on the deposition velocity, for the entire day and separately during daytime and nighttime, as suggested by Fowler et al. (2001). The most important environmental control on the nighttime half-hourly averaged O_3 fluxes was wind speed (Table 1). Wind speed was also highly significant but explained only less than 1% of the variability in the half-hourly averaged nighttime deposition velocity. During daytime, the single most important control on total O_3 uptake was VPD. Wind speed was still an important control, and increased the explanatory power of the model. VPD and wind speed were also significant but only explained very small percentage of the deposition velocity (Table 1).

The official AOT40 reported by VMM in Gent (about 10 km from the research field site) was about 3 ppm h in 2011. At the field site we estimated AOT40 to be 5.6 ppm h from April until the end of October. The cumulative stomatal uptake from April to November, estimated as a daily average uptake for each of the months was about 25 mmol m^{-2}. This value is an underestimation as the stomatal uptake during mid-July to mid-September could not be

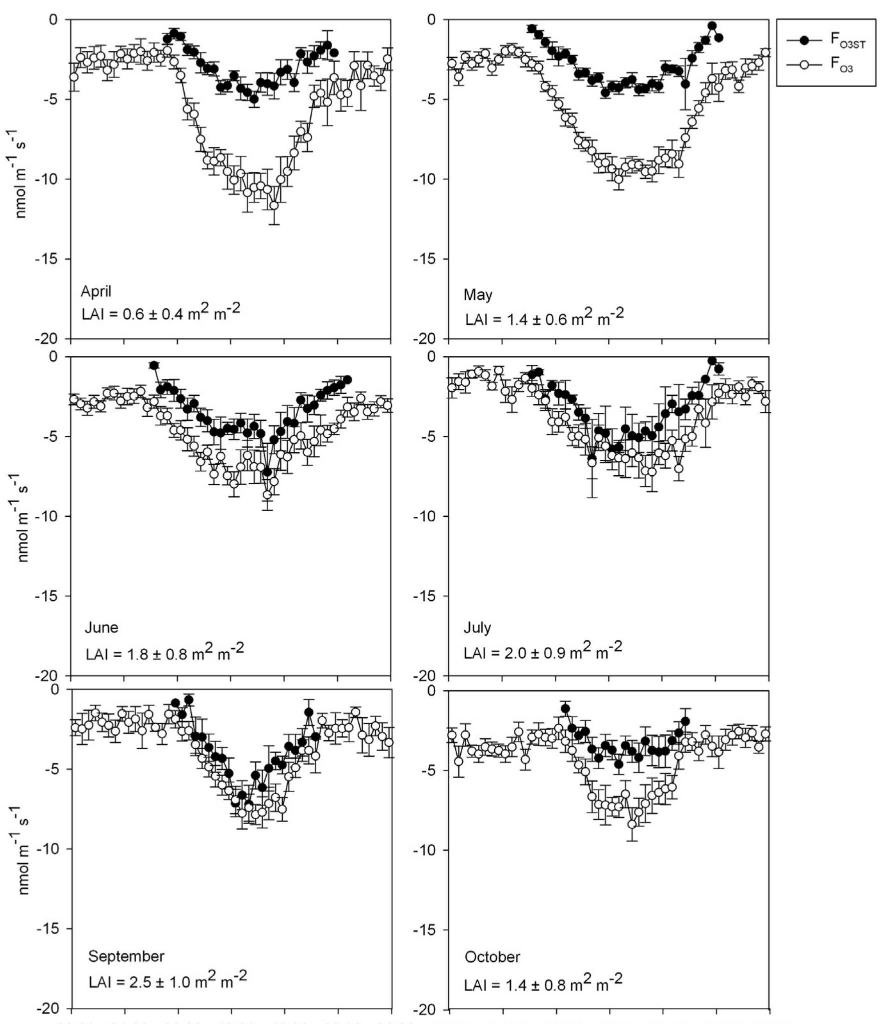

Fig. 5. Diurnal trend of not gap-filled O_3 fluxes (total: F_{O3}; stomatal: F_{O3ST}) for each of the indicated months. Displayed are ensemble averages and standard error of the mean. A monthly average leaf area index (LAI) ± standard errors are displayed in each panel.

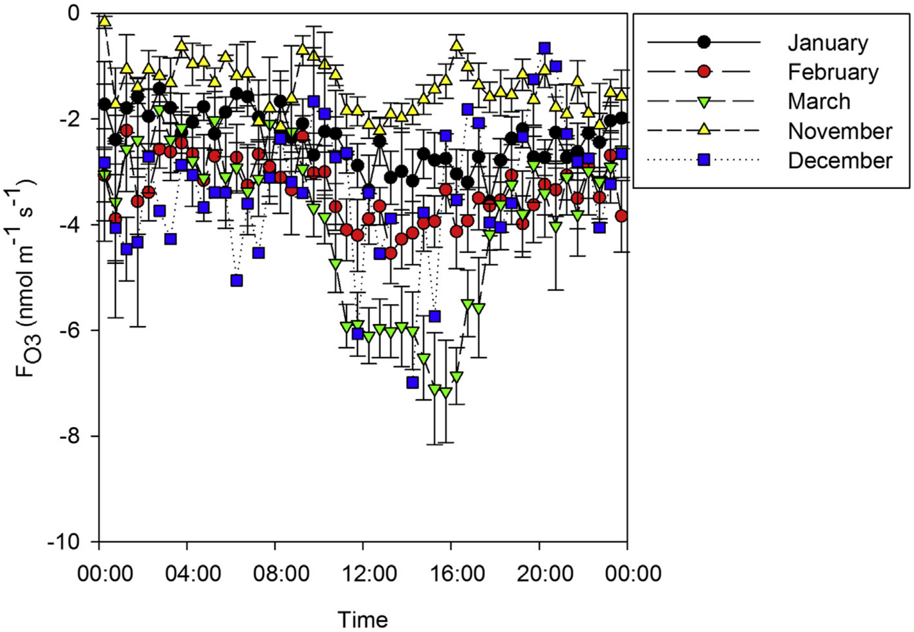

Fig. 6. Diurnal trend of not gap-filled total O_3 fluxes (F_{O3}) for each of the indicated months. The vegetation was not active during these periods (with the exception of November when leaf fall was still occurring). Displayed are averages for the same time of the day and standard error of the mean.

modeled. If the stomatal uptake during this period is assumed to be 59% of the total fluxes (i.e. the seasonal average stomatal ozone uptake), the resulting cumulative stomatal uptake for the entire growing season would be 27 mmol m^{-2}. Multiple regression and partial correlation analysis of the CO_2 flux data from this study showed no impact of O_3 on photosynthesis (Appendix A).

4. Discussion

The comparable O_3 fluxes in January–March (when the vegetation was not active yet), and during most of the growing season (with substantial canopy development), highlights a dominant role of non-stomatal O_3 uptake in this system. The importance of wind speed on O_3 fluxes more than on deposition velocity suggests that the turbulent mixing and the mechanical destruction of O_3 played a role on non-stomatal O_3 fluxes, but not on the surface exchange. Deposition velocity was poorly explained by any models, which suggests that a half-hour time scale might not be appropriate for the investigation of the controls on deposition velocity. A mechanical destruction of O_3 by contact with snowflakes under turbulent conditions (Cieslik, 2009), was probably responsible for the substantial O_3 fluxes observed during the storm at the beginning of February in absence of active vegetation. Ozone deposition to snow has previously been reported (Helmig et al., 2007; Cieslik, 2009; Bocquet et al., 2011) and explained as chemical interaction in the

Table 1
Statistical results (GLM) of the half-hourly averaged not gap-filled total O_3 fluxes and deposition velocity for the daytime and nighttime (solar radiation>20 W m^{-2} or<20 W m^{-2}, respectively) datasets. Displayed are the explanatory powers and the statistical significance (p-values) of the listed variables.

	O_3 fluxes		Deposition velocity	
	Daytime	Nighttimes	Daytime	Nighttimes
Wind speed		44%($p<0.001$)		<1%($p<0.001$)
VPD	38%($p<0.001$)		2%($p<0.001$)	
VPD & wind speed	47%($p<0.001$)		8%($p<0.001$)	

snowpack (Helmig et al., 2007). However, in this field site snow did not deposit on the ground during the peak O_3 flux in February, we therefore assume the mechanical destruction (Cieslik, 2009) was more important than deposition to snow for the observed peak in O_3 fluxes.

The difference between the daytime and nighttime O_3 fluxes was higher from April to May when the F_{O3ST} was the lowest, as the dry condition, particularly during May, limited CO_2 uptake by the vegetation (Zona et al., 2013) and consequently the stomatal ozone uptake. This highlights the importance of non-stomatal uptake during the light hours. A daytime increase in the non-stomatal uptake also occurred when vegetation was not active (most evident in March). This increase has been linked to the daytime increase in [O_3] and the decrease in aerodynamic resistance (Fowler et al., 2001). The observed mismatch between the peak O_3 uptake and maximum [O_3] has already been reported in several ecosystem (Kurpius and Goldstein, 2003; Mikkelsen et al., 2004; Fares et al., 2013), and it is related to delay in the ozone formation through the photochemical process.

Mechanisms leading to O_3 deposition are connected to VOC and NO emission from vegetation and from the soil. The importance of NO as O_3 sink has already been reported by several studies (Wesely et al., 1982; Pilegaard et al., 1998; Dorsey et al., 2004; Michou et al., 2005; Wang et al., 2006). Gas-phase reaction between ozone and BVOC showed to be the major non-stomatal sink in a multitude of crop and forest ecosystems (Kurpius and Goldstein, 2003; Fares et al., 2010b, 2012; Rannik et al., 2012). Certain classes of BVOC, in particular monoterpenes and sesquiterpenes, seem to be associated with the non-stomatal ozone fluxes (Holzinger et al., 2005; Fares et al., 2012; Rannik et al., 2012). On the other hand, emission of BVOC, and isoprene in particular, can also contribute to the O_3 formation (Jacob and Winner, 2009; Beltman et al., 2013). Poplar is known to be a major emitter of isoprene, the most abundant BVOC emitted on Earth by plant ecosystems (Guenther et al., 2006; Jardine et al., 2012). Isoprene production is maximized by light and temperature (Guenther et al., 1993), the same environmental conditions which promote photochemical ozone formation. It is therefore plausible that isoprene might have contributed to enhance [O_3] and ultimately increase the O_3 fluxes. However, additional measurements on BVOC emissions and their oxidation products are required to clarify the mechanisms responsible for the chemical degradation component of non-stomatal O_3 sink.

Critical values (corresponding to a 2–4% biomass loss or growth reduction, ICP, 2004) have been set to 5 ppm h for forests (AOT40), similar to the ones observed at our site. Foliar injury to poplar has been observed for AOT40 equal to or higher than 10 ppm h and for a stomatal ozone uptake equal to or higher than about 30 mmol m^{-2} (Marzuoli et al., 2009). The cumulative O_3 uptake estimated in this study (25–27 mmol m^{-2}) is lower but similar to values linked to visible damage in poplar (between 27.85 and 30.40 mmol m^{-2}, Marzuoli et al., 2009). In agreement with this observation, we did not notice visible damage from O_3 exposure neither on the leaves, nor on NEE. However, a reduction in primary productivity has been shown even without visible damage (Wang et al., 1986). Several poplar species including some of the hybrids used in this study are known to be sensitive to O_3 such as *Populus nigra* (Novak et al., 2007; Bortier et al., 2000) and *Populus trichocarpa* (Street et al., 2011), *Populus maximowizii* × *trichocarpa* (Landry and Pell, 1993), *Populus tremuloides* (Oksanen et al., 2001; Berrang et al., 1991; Karnosky et al., 1992) but these studies usually reported significant impacts with [O_3] much higher (e.g. ≥100 ppb) than the ones observed in this study.

5. Conclusions

Over the entire year of measurements, the non-stomatal O_3 sink was a substantial component of the total O_3 fluxes at our research site. The relative importance of non-stomatal O_3 uptake (as percentage of the total O_3 fluxes) was at its maximum during April–May and during daytime. Deposition velocities were the highest during February and October–November, in absence of a developed canopy. Substantial O_3 deposition was observed during a snow storm, with rates comparable to the ones observed when the vegetation was at peak development. Wind speed represented the most important control on nighttime O_3 fluxes, and therefore on the non-stomatal O_3 sink. Despite the dominance of the non-stomatal O_3 flux, the vegetation still absorbed a considerable amount of O_3, with an average stomatal contribution of about 59% of the total O_3 uptake during the growing season. This uptake, however, did not result neither in any visible damage to the poplar leaves nor caused a reduction in NEE. More studies are needed to explore the individual contribution of stomatal and different non-stomatal pathways and sinks to total ozone removal from the atmosphere in this and other ecosystems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.08.032.

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